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The Atmosphere as a Sink for PCBs

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In this paper, preliminary results of the application of an equilibrium method for determining the Henry's Law Constants (HLCs) for all the individual chlorobiphenyl compounds in the Aroclor® mixtures are reported. Most of the individual compounds in Aroclor 1242 and 1254 have HLCs in the range of 2 to 7×10^{-4} atm-m^3/mol. A method is also described which permits the fugacity of the PCBs in natural waters to be determined. Preliminary results of this method with Lake Michigan water indicates that about 60% of the PCBs in the water samples tested were in true solution.

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ABSTRACT

Preliminary results of the application of an equilibrium method for determining the Henry's Law Constants (HLCs) for all the individual chlorobiphenyl compounds in the Aroclor^{R} mixtures are reported. Most of the individual compounds in Aroclor 1242 and 1254 have HLCs in the range of 2 to 7 atm-m^3/mol. A method is also described which permits the fugacity of the PCBs in natural waters to be determined. Preliminary results of this method with Lake Michigan water indicates that about 60% of the PCBs in the water samples tested were in true solution.

The implication of these results to the sources and sinks of PCBs in natural waters is discussed.

INTRODUCTION

One of the major problems remaining in determining the PCB budgets of the Great Lakes is the question of whether there is net transport of PCB vapor into or out of the water. Conceptually, the problem is a simple one. Given the concentration of PCBs in the atmosphere, lake water, and the equilibrium distribution coefficient (the Henry's Law constant, HLC), the direction of net transfer of

PCBs through the air/water interface can be determined. The amount of PCBs transferred may then be estimated through the use of an available mass transfer model which relates the differences in fugacity to a mass transfer rate.

The problem is that the necessary HLCs and water concentrations have been difficult to determine and reasonable estimates of them are not yet available. This report is a brief discussion of our studies which yield HLCs for individual chlorobiphenyl compounds and for the Aroclor mixtures, and which permit the amount of PCBs in true solution in a water sample to be determined.

Rather than discussing and comparing the concentrations and amounts of PCBs in the air and water phases, its conceptually much easier compare their fugacities. The concept of fugacity, developed by G. N. Lewis, recently has been clarified and promulgated by Mackay (1,2). Fugacity is a measure of the escaping tendency of a material in a particular phase. The attraction for the use of fugacity is that for a material distributed between two or more phases, and at equilibrium, the fugacity of the material in each phase is the same. In contrast, the concentrations or amounts of the material in each of the phases at equilibrium will be different, with the amounts present related to the fugacity factor (Z) for the material in that phase. For a system not at equilibrium, transport will be in the direction to equalize the fugacities.

The fugacity of a material in a phase is proportional to the concentration of the material divided by the capacity factor (Z) for that material (1). The fugacity of vapor phase materials is relatively easy to determine. It is equal to the vapor pressure of the material (atm). The fugacity of a material in the liquid phase is equal to the amount in solution (mol/m^3) times the Henry's Law Constant ($atm\text{-}m^3/mol$), for that material.

HLC's for Chlorinated Biphenyls and Aroclor Mixtures

The HLCs are required in order to calculate the fugacity of the PCBs in the water phase. Also, as will be seen, they are needed to determine the percent of the total PCBs in a water sample that are in solution. Unfortuately, the HLCs for PCBs are not well known. A recent article (3) discussing this problem shows a range of 10^4 for the partition coefficient of Aroclor 1242. Some of the reasons for this are that the low vapor pressure and solubility of the individual compounds at room temperature makes their determination difficult. The fact that essentially all of

the pure chlorinated biphenyl compounds are solids at room temperature while the commercial mixtures are liquids also complicates this determination. Finally, since more than 100 of the 209 possible different compounds do occur in the commercial mixtures, the need to determine all the individual HLCs is a formidable task.

The method used in this project to determine the HLCs for PCBs involves the preparation of saturated solutions of some of the individual chlorinated biphenyl compounds and commercial PCB mixtures. The solutions were prepared by the method of Haque and Schmedding (4). The material to be dissolved was placed on the bottom of a clean, 4-liter glass bottle, about 3 liters of clean, organic-free water was added [the water was prepared with a Millipore Super-Q^{R} system and then passed through XAD-2 resin, or deionized water was refluxed for 24 hours with acid dichromate and then distilled through an all-glass, packed column], and the solution stirred for one to two months. The solution was then permitted to stand undisturbed for at least two additional months to come to equilibrium.

The water phase was sampled by taking two ml of water from beneath the surface with a pipet which had been equilibrated with some of the solution. The water was added to a vial containing 0.200 ml of isooctane. The vial was shaken to extract the water, and the amount of PCBs in the isooctane was determined by gas chromatography with an electron capture detector (GC/ECD).

The container with the solution of the PCBs was covered with aluminum foil and permitted to stand undisturbed for several days. A sample of the vapor was collected by puncturing the foil with a glass, disposable pipet containing about 0.5 gm of Florisil^{R}. A measured volume of air (usually 50 or 100 ml) was drawn through the pipet. The chlorobiphenyl compounds collected on the Florisil were eluted with hexane, and the amount present determined with GC/ECD. The volume of air collected was corrected for the dilution which occurred as air was drawn into the container being sampled.

The use of capillary gas chromatography to determine the amounts of each of the chlorinated biphenyl isomers present in the vapor and water phases of an equilibration of one of the Aroclor mixtures, permits the HLCs for ALL of the chlorinated biphenyl isomers present in measurable amounts in both phases to be determined simultaneously. Also, since excess Aroclor is present, the solution is saturated with

respect to the Aroclor. If the Aroclor composition is known, then the vapor pressure and water solubility of each of the chlorinated biphenyl isomers may also be calculated.

This determination assumes that all of the PCBs present in the water phase are in solution. Low HLC values would result if any PCBs are present on particles. To minimize problems with particulates, clean, organic-free water was used to prepare the solutions. As a check, the concentrations of PCBs found in all of the solutions were in close agreement with the reported water solubility of the PCB used.

The results of the capillary gas chromatographic (GC) determination of the HLCs of the chlorinated biphenyl compounds in Aroclor mixtures are shown in Table 1. HLCs with two different units are shown. While the HLCs reported in Table 1 for the components of the Aroclors may have an error of a factor of 2 to 3 associated with them at this time, the relative HLCs of the individual compounds should be reasonably accurate. It is remarkable how similar the HLCs are for the individual compounds. The differences between most of them are not statistically significant. It is also interesting to note that the HLCs tend to increase for the higher molecular weight compounds. This indicates that the solubility of the compounds decreases faster as more chlorines are substituted on the biphenyl molecule, than does the vapor pressure.

Henry's Law Constants for three chlorinated biphenyl compounds were determined both on solutions of the single isomers and on solutions of the Aroclor mixtures. These results are summarized on Table 2 along with some information on particular batches of two Aroclors and information from the literature on individual chlorobiphenyl compounds. Most of the measurements on the solutions of the single isomers were made with packed column GC, and the results were in close agreement with those made with capillary GC. There is very good agreement between the literature values for the 2,2',5,5'-tetrachlorobiphenyl and the values found in this project.

There is a difference in all three cases studied, however, between the HLC for a specific compound determined on a solution of the individual compound versus a determination made on a solution of an Aroclor mixture containing that compound (Table 2). This difference could imply that the activity of a PCB compound is different in a solution of the pure compound than in a solution prepared from the Aroclor. More probably, however, it reflects the experimental error in these determinations at this time.

Water Phase Fugacity of PCBs in Lake Michigan

The difficulty in determining the water phase PCB fugacity arises for several reasons. The major one is that PCBs are mixtures of a large number of compounds, and thus PCB mixtures do not have a true HLC, but rather each PCB compound has an HLC, and the particular PCB mixture present has some "apparent HLC". This apparent HLC presumably varies through time due to preferential gain or loss of component compounds. In addition, the low solubility and vapor pressures of the many of the individual PCB compounds makes the determination of these properties for these compounds difficult. Finally, the fugacity of PCBs in water depends on the amount in true solution, rather than the total amount present in the water. Since much of the PCBs in the water may be associated with small organic or inorganic particulates, it is difficult to determine the amount in true solution.

The method used to determine the fugacity of the PCBs in a water sample involves the use of a solution of an individual chlorinated biphenyl compound whose HLC is known. The procedure is as follows:

1) The total amount of PCBs in a water sample is measured. A solution of a single chlorinated biphenyl compound is added to the water sample. The sample is stirred until equilibrium is attained between the compound in the water and vapor phases.

2) The concentration of this compound in the vapor is measured. This gives its vapor fugacity and also its water fugacity (they are equal at equilibrium). The concentration of the compound in solution in the water is calculated (fugacity/HLC).

3) The total concentration of the chlorinated biphenyl compound in the water is measured, and the ratio of the concentration of the compound in solution to the total amount in the water is calculated.

4) This ratio is multiplied by the total amount of PCBs originally found in the water sample to determine the amount in solution in the water.

These determinations were made by adding a solution of 2,2',5-trichlorobiphenyl (TCB) to about 5 liters of lake water in a 20 liter container. After several days, a sample (~10 liters) of vapor was collected along with a sample of the water (~10 ml) and their TCB concentrations determined. The fugacity of TCB in the vapor phase is equal to its vapor pressure in the atmosphere. The concentration of the PCBs

in true solution in the water then is its fugacity (which is equal to the fugacity of the vapor) divided by the HLC for TCB (3.5×10^{-4} atm-m^3/mol). This amount when divided by the total TCB in solution, gives the fraction of the TCB in true solution in the water. This fraction is assumed to hold for the PCBs originally present in the solution. From the total concentration of PCBs determined on the original sample, and this fraction, the fugacity of PCBs in the water sample can be calculated. The fugacity of PCBs in three samples of inshore Lake Michigan water was 59% of the total PCB concentration in the water. The calculations for one of these samples is shown in Appendix A.

The Direction of PCB Movement Across the Air/Water Interface

For a total PCB concentration in Lake Michigan of 2×10^{-8} mol/m^3 (5 ng/l), a HLC of 2×10^{-4} atm-m^3/mol and 59% of the total PCBs being dissolved, the water phase fugacity of PCBs is 2.4×10^{-12} atm. This is an order of magnitude higher than the fugacity of PCBs in the atmosphere over Lake Michigan of 1.6×10^{-13} atm (1 ng/m^3)(3). These results indicate that the net movement of PCB vapor is from the water to the atmosphere. Estimates of the amounts transferred indicate that it could be substantial (3).

While the concentration of the chlorobiphenyl compound used to determine the fugacity of PCBs in the aqueous phase (Appendix A) is a factor of 50-100 higher than the concentrations normally found in the Great Lakes, it should still be low enough that the nature of the interactions between the dissolved and particulate phases is not substantially changed.

It should be pointed out that the presence or absence of a surface film and its chemical nature, or loss to the walls of the container should have no effect on these measurements if care is taken to exclude the surface layer when the bulk water is sampled. This is because the system is sampled at equilibrium when the fugacity of PCBs in all of the phases present is equal. While the concentrations of PCBs may be considerably higher in a surface film, this just means that the fugacity capacity (Z) for PCBs of this phase is higher than that of water. This, in fact, would be expected since the microlayer is known to be less polar in nature than is water, and it is different enough chemically to be physically separate from the water phase.

Determinations of the HLCs for Aroclors and chlorobiphenyl compounds reported here are mostly in the range of 2 to 7×10^{-4} atm-m^3/mol. The ramifications of this with

respect to atmospheric deposition are as follows. A water concentration of 1 ng/l of a PCB with an HLC of 3.3×10^{-4} atm-m^3/mol will support a vapor PCB concentration of 13.3 ng/m^3. Thus, precipitation in equilibrium with an atmospheric vapor concentration of 2 ng/m^3 of PCB, will have a dissolved PCB concentration of 0.15 ng/l. This is a concentration two orders of magnitude or more lower than is normally found in precipitation (7), and indicates that vapor scavenging can account for less than 1% of the wet deposition PCB inputs. This is in agreement with experimental findings (8,9) that the PCBs scavenged by precipitation come mostly from particulates.

The results reported here for the HLCs were made on experiments where the temperature of the water was not carefully controlled. Also, only a few replicate determination were made. More careful measurements are now being made on solutions at constant temperature; on solutions at different temperatures; and on solutions at concentrations other than at saturation. The results of these experiments should give better data on the HLCs of concern for environmental transport needs.

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Table 1. Henry's Law Constants for PCBs

Compound	Compound Identity Number(10)	HLC (atm-m^3/mol) X 10^4	HLC (ng/m^3) ng/l
22'	4	2.2	9
(23')	(6)	2.1	8.8
(24')	(8)	2.2	9
(22'6)	(19)	2.1	8.8
22'5	18	2	8.3
44'+22'3	15+16	3	12.3
Unknown		1.4	5.8
Unknown		2.4	10
(23'4)	(25)	1.6	6.5
24'5	31	2	8
2'34	33	1.5	6.2
22'56'	53	3	12.8
234'	22	1.8	7.6
Unknown		2	8.3
Unknown		2.2	9
22'55'	52	2.2	9
22'45'	49	2	8.4
22'44'+ 244'6	47+75	3.7	15
22'35'	44	2.4	10
23'4'5	70	2	7.6
22'345'	87	3.3	13.5
(233'4'6)	(110)	3.7	15
22'33'4	82	2	7.6
22'355'6	151	3	12
22'345'6	144	6	25
Unknown		5	21
22'34'5'6'	149	3	12
23'44'5	118	4	15
22'33'56	134	5.7	23
22'44'55'	153	3.5	14
22'3455'	141	4	16
22'344'5	138	4.8	20
Unknown		6	24
22'344'5'	138	4.8	20
233'44'6	158	6.4	26
Unknown		11	46
Unknown		7.3	30
22'344'5'6	183	6.3	26
22'33'44'	128	5	20.6
22'33'4'56	177	22	90
233'44'5	156	8.7	36
233'44'5'	157	5.8	24

Table 2. Henry's Law Constants for Chlorobiphenyl Compounds and Aroclor Mixtures from Equilibrium Measurements

Source	HLC ($atm-m^3/mol$) $X10^4$	HLC ($Pa-m^3/mol$)	HLC ($\frac{ng/m^3}{ng/l}$)
2,2',5-Trichlorobiphenyl			
Single Isomer (3)*	3.4	35	14.3 ± 2.7
Aroclor 1242 (3)	2	20	8.3 ± 2.7
2,2',5,5'-Tetrachlorobiphenyl			
Single Isomer (3)	2.6	27	10.8 ± .54
" "	3.1-5.3	30-55	13-22 ref. (5)
" "	2.8	28	11.5 ref. (6)
Aro 1242 & 1254 (3)	2	21	9 ± 5.7
2,2',4,4',5,5'-Hexachlorobiphenyl			
Single Isomer (3)	2.7	27	11 ± 1.7
Aroclor 1254	3.5	35	14
Aroclors			
Aroclor 1242 (3)	2.2	23	9 ± 4.5
Aroclor 1254	2	21	8.4

*Number of determinations

Appendix A. Determination of the Fugacity of PCBs in Lake Michigan

2,2',5-Trichlorobiphenyl (TCB); HLC = 3.5×10^{-4} $atm-m^3/mol$

1111 ng added to 4.5 liters of Lake Michigan water in a 20 liter container

Air concentration determined = 2220 ng/m^3
= 2.1×10^{-10} atm

Total measured water TCB concentration = 260 ng/liter
= 1×10^{-6} mol/m^3

TCB concentration in the water in equilibrium with the vapor = $\frac{2.1 \times 10^{-10} \text{ atm}}{3.5 \times 10^{-4} \text{ atm-m}^3/\text{mol}} = 0.6 \times 10^{-6} \text{ mol/m}^3$

TCB in solution = $\frac{0.6 \times 10^{-6}}{1 \times 10^{-6}} \times 100$ = 60 percent of total